Bioresource Technology 143 (2013) 139–146

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Hydrothermal carbonization: Process water characterization and effects of water recirculation

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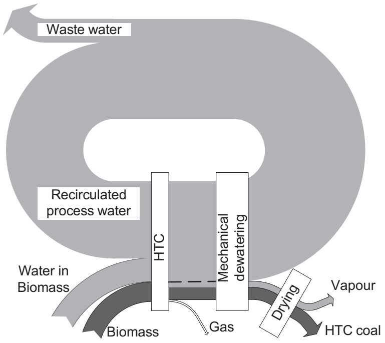
HIGHLIGHTS

- Poplar wood was treated hydrothermally at 220 °C and process water was analyzed.
- Polar, aromatic compounds, and substances of higher molecular weight were detected.
- Accumulated organic acids in the liquid phase catalyze dehydration reactions.
- Recirculated reactive compounds polymerize and form additional solid substance.
- Overall process performance is greatly enhanced by recirculation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 April 2013
Received in revised form 24 May 2013
Accepted 25 May 2013
Available online 2 June 2013

Keywords:
Dissolved organics
Accumulation
Polymerization
Organic acids
Energetic yield

ABSTRACT

Poplar wood chips were treated hydrothermally and the increase of process efficiency by water recirculation was examined. About 15% of the carbon in the biomass was dissolved in the liquid phase when biomass was treated in de-ionized water at 220 °C for 4 h. The dissolved organic matter contained oxygen and was partly aerobically biodegradable. About 30–50% of the total organic carbon originated from organic acids. A polar and aromatic fraction was extracted and a major portion of the organic load was of higher molecular weight. By process water recirculation organic acids in the liquid phase concentrated and catalyzed dehydration reactions. As a consequence, functional groups in hydrothermally synthesized coal declined and dewaterability was enhanced. Recirculated reactive substances polymerized and formed additional solid substance. As a result, carbon and energetic yields of the produced coal rose to 84% and 82%, respectively.

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1. Introduction

1.1. Background

To date wet lignocellulosic biomass cannot be converted to a fuel with satisfying efficiency using conventional technologies as gasification or pyrolysis. Hydrothermal carbonization (HTC) may be an efficient pre-treatment process to produce a solid lignite-like fuel. For hydrothermal treatment biomass is covered with hot water and is heated to around 200 °C in a pressurized vessel (Erlach et al., 2012). The solid product has a high calorific value and good dewatering properties which make it favorable for combustion, pyrolysis (Chang et al., 2013), and gasification (Tremel et al., 2012).

Hydrothermal treatment in an industrial scale was first applied for dewatering of lignite and peat and now is mainly used for decomposition and solvolysis of biomass in several industries (Toor et al., 2011). Recently the use of the solid product as a soil additive and a carbon sink was proposed (Titirici et al., 2007). However, because of its chemical similarity to lignite, the solid

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http://dx.doi.org/10.1016/j.biortech.2013.05.098

product can also be used as fuel and HTC is discussed as a pre-treatment technology similar to torrefaction (Yan et al., 2009; Stemann et al., 2012). Since high pressure is applied during the process, water does not have to be evaporated which makes the process well applicable to wet biomass and especially residual resources. Biomass constituents are degraded during the process which enhances pulverization and fluidization properties and may allow for large scale entrained flow gasification after HTC (Tremel et al., 2012).

1.2. Substances

During the process a solid, liquid and gaseous phase is formed. For moderate temperatures of 220 °C and a water to biomass ratio of 5, approximately 80% of the carbon is recovered in the solid phase, 5% in the gas phase and 15% are dissolved in the liquid phase. Several authors propose the addition of acid as catalyst (Antonietti, 2006; Lynam et al., 2011).

Many experiments have been performed with model compounds in order to describe reaction pathways and kinetics (Antal et al., 1990; Bobleter, 1994; Kabyemela et al., 1999; Kamio et al., 2008; Kuster, 1990; Ruiz et al., 2013). The following simplified reaction pathways are known for the main constituents of biomass: (1) Cellulose hydrolysis initially forms oligosaccharides and subsequently monomeric glucose. This isomerizes and forms fructose which then dehydrates and forms hydroxymethylfurfural (HMF). The latter subsequently is assumed to polymerize to char, or may also rehydrate to levulinic and formic acid. (2) Hydrolysis of hemicellulose initially forms oligosaccharides and subsequently monomeric xylose which then dehydrates and forms furfural which subsequently polymerizes. (3) Lignin forms several phenols which, however, readily polymerize.

When real biomass is treated hydrothermally instead of the above mentioned model compounds, the substances in the liquid phase which can be detected with chromatography are mainly organic acids but also further intermediate products such as HMF, furfural, phenol and monomeric sugars. In addition compounds of higher molecular weight are dissolved in the liquid phase. Knežević et al. (2009) detected dissolved substances with mole masses of up to 10,000 g/mol with polystyrene calibrated size exclusion chromatography (SEC), but SEC of hydrated molecules may overestimate molecular weight.

1.3. Environment

For acid hydrolysis of cellobiose it is known that cleavage of glycosidic bonds is catalyzed by hydronium ions whereas for hydrothermal treatment a pH independent range of 3–7 is assumed (Bobleter, 1994). This is because no autocatalyzation of cellobiose decomposition by organic acids was detected which are formed during the reaction (Bobleter and Bonn, 1983).

Yet, an autocatalytic effect of acetic acid on ester hydrolysis is reported (Krammer and Vogel, 2000), and a catalytic effect of formic acid and acetic acid on fructose is described (Li et al., 2009). Lynam et al. (2011) observed a rise of the calorific value and propose that higher concentrations of organic acids cause a higher reaction severity similar to higher temperatures.

Phase yields and composition mainly depend on the reaction severity and thus mainly on the temperature applied during the process. Generally higher temperatures cause a lower solid mass yield and an increment in calorific value (Funke and Ziegler, 2010; Parshetti et al., 2013; Yan et al., 2009). The hydrothermal reaction is very sensitive to the applied temperature around 220 °C. One explanation for this phenomenon may be the considerable decrease of intermolecular hydrogen bonds in cellulose fibers at 220 °C (Watanabe et al., 2006).

1.4. Recirculation of water

In an industrial scale it probably is not economical to add rather valuable organic acids in order to produce a solid fuel rather low in economical value. However, it is obvious that recirculation of process water may be easily feasible to increase acidity and may come along with a series of advantages:

(1) The amount of waste water can be reduced significantly which would reduce waste water treatment costs. (2) Moreover, simulations show that recirculation of hot compressed water may be an efficient means of heat recovery and thus reduce external heat consumption tenfold (Stemann and Ziegler, 2011). (3) Also carbon and energetic yields may slightly rise by further polymerization of dissolved organic substances. (4) Finally, the concentration of organic acids in the water is expected to raise the heating value and carbon concentration of the solid, and thus increase energy density.

The amount of water which can be recirculated mainly depends on the water content of the feed biomass and the water to biomass ratio applied during the process. For recirculation the solid and liquid phase must be separated mechanically and no additional makeup water is necessary.

In order to use the solid product as a fuel in combustion or gasification, extensive dewatering is crucial, as drying of pre-treated char is expected to require second most energy next to preheating of biomass (Erlach et al., 2012).

Thermal treatment is expected to destroy oxygen containing functional groups at which water is adsorbed. For lignites a linear relation between O/C ratio and water content was found (Ruyter, 1982). For HTC derived coals, equilibrium moisture content is reduced when higher temperatures are applied during the HTC treatment, yielding lower O/C ratios (Yan et al., 2009).

The aim of this work is to characterize HTC process water based on sum parameters as well as on a molecular level and to explore and explain effects of water recirculation on liquid, solid, and gaseous yield and composition.

2. Experimental

2.1. Materials

Dry poplar wood chips with a size of 5 mm were acquired from Fa. Uwe Wagner, Seligstädt (Germany). Just enough water was added to the biomass so that is was submerged in order to allow for homogenous reaction conditions for the biomass in the reactor. This resulted in a mass ratio of water to biomass of 5. Therefore 100 g of liquid were added to 20 g of dry wood. For the reference experiments, referred to as *HTC-Ref*, de-ionized water was used and experiments were repeated at least three times.

In the recirculation experiments, instead of fresh water, first water from a reference experiment and then subsequently water from each previous experiment was used. In order to account for the fact that fresh forest wood contains approximately 55% water, 24.44 g of de-ionized water was added to dry wood. Then 75.56 g of process water were added to reach 100 g of total liquid. This procedure is similar to submerging fresh, wet wood into recirculated water. This recirculation type experiment is referred to as *HTC-Recirc*. With always fresh dry wood the process water was used in 4 subsequent experiments for general water characteristics and 19 times for assessing equilibrium behavior. The experiments showed that mass yields and composition changed significantly during the first five runs of the recirculation experiments. Thereafter no further significant changes were observed and, after reaching equilibrium and where applicable, results from experiments were aggregated for statistical analysis. Drying of wood releases volatile organic compounds as e.g. monoterpenes. Thus adding water to a dried wood sample in comparison to freshly harvested wood may result in a small deviation but effects on the HTC reaction and the main findings were assumed to be minor and were not assessed in detail.

Additional experiments were conducted in order to study the effect of dissolved organic acids in recirculated process water on the HTC reaction. The amount of acid was chosen to be the same as in 75.56 g of recirculated water after reaching equilibrium. Therefore 2.50 g of acetic acid, 0.50 g of glycolic acid and 0.23 g of formic acid were added together with 96.77 g of de-ionized water to the biomass prior to heating. The experiments were repeated three times without recirculation and were compared with three reference experiments.

2.2. Experimental procedure

The sample was heated to 220 °C in a Berghof BR-200 reactor with a PTFE liner and a volume of 200 mL. Prior to heating the reactor was purged with nitrogen. The temperature was controlled by a PID controller and held at 220 °C for 4 h. It took 35 min for the reactor to reach 180 °C and 70 min in total to reach 220 °C. Cooling from 220 °C to 180 °C took 25 min. These times are important because below 180 °C (the temperature above which hemicellulose, the least stable fraction in biomass, begins to decompose) the reaction is not significant anymore.

2.3. Phase quantification

After cooling to room temperature one valve of the reactor was completely opened for three minutes, gas was collected in a sample bag, and its volume was determined. In a first step the solid and liquid were separated by vacuum filtration with 8 μm cellulose filter paper. Afterwards the solid phase in the filter paper was transferred to a laboratory piston press and the solid was mechanically dewatered at 10 MPa for 5 min. Dewatering the HTC coal mechanically to a large extent was important in order to obtain liquid for water recirculation and subsequent analysis. The solid was removed from the filter paper after dewatering and was dried at 105 °C for 24 h for quantification of the solid mass.

2.4. Analytics

All chemicals used were analytical grade. The samples were stored in a refrigerator until analysis. Before analysis the samples were diluted from 1:60 up to 1:5000, depending on the requirements for the analysis. About 98–99% of the carbon in the biomass was recovered in the solid, liquid and gas phase.

2.4.1. Liquid phase

For the characterization of the process wastewater the following parameters were determined: pH (WTW, Weilheim, Germany), total organic carbon (TOC, HighTOC, Elementar, Hanau, Germany), chemical and biological oxygen demand (COD, BOD), UV absorbance at 254 nm (Lambda 12 dual beam spectral photometer, Perkin Elmer, Rodgau, Germany). For COD determination the Hach-Lange cuvette test was used as well as an oven and a photometer from Hach-Lange (Düsseldorf, Germany). The BOD was determined with an OxiTop® system (respirometric BOD, WTW, Weilheim, Germany). Sample preparation and filling of the measuring bottles were done according to DIN 38409 H52. The samples were inoculated with an effluent of a waste water treatment plant (Ruhleben, Berlin, Germany). Size exclusion chromatography with continuous UV and online organic carbon detection (LC-OCD, DOC-Laboratory Dr. Huber, Karlsruhe, Germany) was used to characterize the dissolved organic carbon. For separation a Toyopearl HW-50S column (250 × 20 mm, Tosoh Bioscience, Tokyo, Japan) and as mobile phase a phosphate buffer (20 mM) at a flow rate of 1.0 mL/min was used. After separation and detection of the UV absorption (254 nm) the mobile phase passed through a Gräntzel thin film reactor where the organic compounds are oxidized after the addition of concentrated phosphoric acid (0.4 mL/min) and irradiation with UV light at 184 nm. The produced carbon dioxide was transferred into an infrared detector with nitrogen as the carrier gas.

Selected small organic compounds were quantified by HPLC analysis. 20 μL of sample was injected to 0.01 N sulphuric acid at 0.6 mL/min onto a nucleogel sugar column (Macherey Nagel 810 h, 300 mm × 78 mm) at 80 °C. The compounds were detected by UV-absorbance at 254 nm and retention times were compared with standards. Aliquots of the water samples (3 mL) were extracted with dichloromethane (2 × 30 mL, 2 × 20 mL) and then fractionated by column chromatography (1.6 × 30 cm) with silica gel 100 (16 g). After transferring the extract onto the column the compounds were eluted with (1) n-hexane (40 mL), (2) n-hexane/dichloromethane (9:1, v:v, 60 mL) and (3) dichloromethane/methanol (9:1, v:v, 80 mL). The extract as well as the three fractions were dried, weighed, re-dissolved and then analyzed by GC–MS (Hewlett Packard G1530A; Agilent 5973; CTC auto-sampler; DB5 column, 30 m; splitless injection) without derivation.

2.4.2. Solid and gas phase

Ultimate analysis (CHNS) of the dry solid substances was carried out with a Vario EL III elemental analyzer (Elementar, Hanau, Germany). Ash was determined according to EN 14775. Oxygen was assumed to be the remaining mass. The calorific value (HHV) was calculated in analogy to Channiwala and Parikh (2002). For IR-spectrometry, transmission of pulverized solid samples was analyzed (PerkinElmer Spectrum one, 16 scans, resolution 4 cm^{-1}). Gas composition was analyzed with a HP5890 with packed columns (molesieve and a Porapak QS column, 2 m × 1/8") and a TCD detector.

3. Calculation

In reference experiments with de-ionized water a specific concentration c_0 was determined for each identified substance. When water was recirculated the dissolved substances concentrated. The concentration trend depended on the fraction f of recirculated water $m_{w,r}$ in relation to the total amount of water $m_{w,t}$ after the reaction which was defined by the following equation

$$f = \frac{m_{w,r}}{m_{w,t}} \tag{1}$$

During the HTC reaction 5 g of liquid were formed and thus $m_{w,t}$ = 105 g. As described in Section 2.1, 75.56 g of liquid was recirculated and thus f = 72%. The concentration c_n after n cycles was calculated with the following approach

$$c_n = c_0 + f \cdot c_{n-1} \tag{2}$$

Here c_0 was the concentration of a substance in the liquid after a reference experiment in which only de-ionized water was used. Therewith in Eq. (2) an ideal case was assumed where the amount of substance which dissolved newly from the parent biomass was not affected by its accumulation.

The accumulation ratio r of the concentration found in the experiments $c_{n,exp}$ and the calculated concentration $c_{n,calc}$ was expressed according to

$$r = \frac{c_{n,\text{exp}}}{c_{n,calc}} \tag{3}$$

Values of $r \neq 1$ were interpreted as a deviation from the ideal accumulation behavior.

4. Results and discussion

4.1. Process water

4.1.1. Process water characterization

In order to characterize the process water, a series of parameters were assessed (Table 1). The pH of the process water in general was acidic (~pH 3.5). The COD increased similarly to the TOC to a concentration of 101 g/L COD after 4 cycles. The BOD given was measured after 10 days of incubation of the 1:1000 diluted samples. The BOD_{10} from both sample HTC-Ref (the reference experiment with de-ionized water only) and sample HTC-Recirc4 increased with dilution (1:62.4, 1:100, 1:1000), indicating that some toxic compounds inhibited the biodegradation (data not shown). The hardly aerobically biodegradable fraction might be indicated by the very high UV absorption at 254 nm, representing toxic aromatic substances but a considerable part of the TOC was aerobically biodegradable. The ratios of COD/TOC and UV_{254}/TOC generally decreased, meaning that the oxygen content and the aromatic structure (see below) of the water soluble organic compounds decreased with recirculation in relation to the TOC. The sum parameters clearly show that the process wastewater is heavily contaminated/loaded and needs special treatment.

Size exclusion chromatography with online UV and organic carbon detection was used to characterize the TOC further. Size exclusion chromatography separates by molecular size of the *hydrated* molecules. This fact makes the interpretation of such chromatograms difficult. In order to assign the observed peaks to certain groups of compounds, model substances were injected (data not shown). It was assumed that signals at 55–60 min and 60–65 min (Fig. S-1 in supplementary information) represented organic acids and higher molecular weight compounds with UV activity, because organic acids do not contribute to the UV signal. The fact that the UV signal area was 2.3 times larger after the 4th recirculation than in sample HTC-Ref, indicates that compounds of higher molecular weight concentrated by water recirculation. Such substances similar to humic or fulvic acids may compose a critical subgroup as it can be expected that they decompose slowly during biological water treatment. They may contribute to a high COD level after water treatment, making it difficult to meet legal limits for water discharge. One solution to this problem may be a concentration of these substances by membranes. Recirculation of these substances to the process may cause the formation of additional solid substance.

The area of the organic carbon signal at 60–65 min of sample 4 was 3.2 times higher than in the reference sample, indicating complete accumulation. Small aromatic compounds, like phenol and HMF, which were detected by GC–MS (see below), did not contribute to the signal at 55–60 and 60–65 min, which supports that polar higher molecular weight compounds were responsible for these signals. These higher molecular weight compounds are most probably produced by polymerization of aromatic compounds, e.g., detected by GC–MS.

To get an idea about the organic matter on a molecular level, organic compounds were extracted from the process water with dichloromethane. The extraction yield increased with recirculation from 6.9 to 16.6 g/L (Table 2). The organic carbon content of the extracts was calculated under the assumption that the average elemental formula of the organic compounds was $C_6H_6O_6$. Based on this assumption less than 20% of the TOC was extractable. The first (n-hexane) and second (n-hexane/dichloromethane) fraction after column chromatography were not weighable. 63 ± 5% of the whole extract was found in the third, polar fraction (dichloromethane/methanol). The remaining 40% were most probably caused by polar polymers adsorbed onto the silica gel, visible as a yellow band on top of the silica gel. The polar fraction was analyzed by GC–MS. The total ion chromatogram of sample HTC-Ref was characterized by an unresolved complex mixture (UCM, data not shown). Phenol, 2-methoxy-phenol, 5-hydroxymethylfurfural and 2,6-dimethoxyphenol were the only compounds which were identified. The UCM of sample 4 was resolved a bit better and 2-hydroxy-1-methyl-cyclopentene-3-on and 1-cyclohexylethane-1-on were identified additionally. The ratio of the amount of extract to TOC as well as that of the amount of the polar fraction to the TOC was nearly equal for all samples, indicating that the main composition of the extractable organic matter did not change with recirculation and was polar and aromatic. It seems that the complexness of the UCM was reduced with recirculation, most probably due to polymerization of those compounds ending up in the solid phase of the HTC which is in agreement with the decreasing COD/TOC and UV_{254}/TOC ratios.

4.1.2. Accumulation and equilibrium concentration

In order to examine the progressing concentration and reveal equilibrium concentrations, an experimental series was performed in which the process water was recirculated 19 times. Fig. 1 shows the concentration of total organic carbon (TOC) for the recirculation experiments. The calculated values were computed according to Eq. (2) using the mean value $c_0 = 14.52 \pm 0.31$ of five reference experiments. The load of organic compounds (TOC) was enormous and increased with recirculation as expected. It can be noted that the determined TOC concentration augmented during the first five recirculations and thereafter leveled off, showing the theoretical asymptotical behavior. A comparison of the experiments with the calculated values reveals a good agreement of the general trend towards equilibrium but at a lower TOC level. The accumulation ratio of the experimental concentration to the calculated concentration (mean values of the last three runs each) is only 66%.

It is assumed that recirculated soluble intermediates took part in polymerization reactions and formed additional solid substance. An increment of the concentration of reactive substances may have accelerated the rate of polymerization. This is known for HMF production from fructose, where polymerization reactions and char formation lower the HMF yield at high concentrations (Kuster, 1990). Chuntanapum and Matsumura (2009) report a reaction order of 4.3 for the production of char from HMF. This may indicate

Table 1

pH, sum and group parameters (TOC: total organic carbon, COD: chemical oxygen demand, BOD: biological oxygen demand, UV absorption) as well as ratios to characterize the process water and the recirculation.

Sample	pH	TOC (g/L)	COD (g/L)	BOD_{10}[a] (g/L)	UV_{254} (1/m)	COD/TOC (mgO_2/mgC)	UV_{254}/TOC
HTC-Ref	3.4	17.4	50	24	23.1	2.8	1.3
HTC-Recirc1	3.3	25.1	72	n.d.	24.5	2.8	1.0
HTC-Recirc2	3.3	33.0	82	n.d.	28.7	2.4	0.9
HTC-Recirc3	3.4	33.7	91	n.d.	31.2	2.7	0.9
HTC-Recirc4	3.4	39.2	101	55	27.2	2.5	0.7

n.d. Not determined.

[a] Dilution 1:1000.

Table 2
Amount of the extract and the polar fraction and ratio to the TOC.

Sample	Extraction yield (g/L)	Extractable organic compounds as part of TOC (%)[a]	3rd fraction (g/L)	3rd fraction as part of the extraction yield calculated as TOC (%)
HTC-Ref	6.9	16	4.5	65
HTC-Recirc1	12.9	21	6.8	53
HTC-Recirc2	13.2	17	7.8	59
HTC-Recirc3	14.9	18	10.2	69
HTC-Recirc4	16.6	17	10.8	65

[a] Assumption: the average elemental formula of the organic compounds is $C_6H_6O_6$.

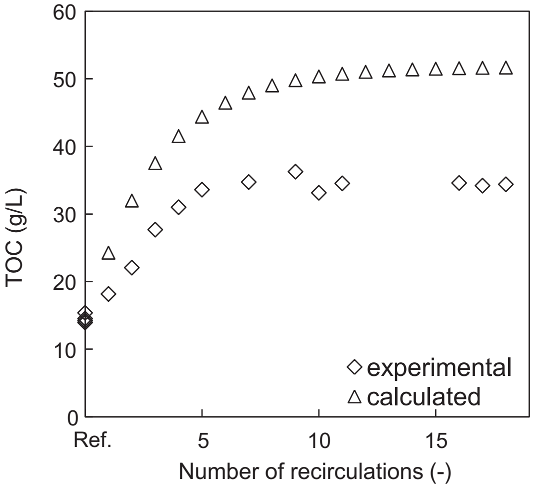

Fig. 1. Experimental and calculated total organic carbon concentration (TOC) for the number of process water recirculations.

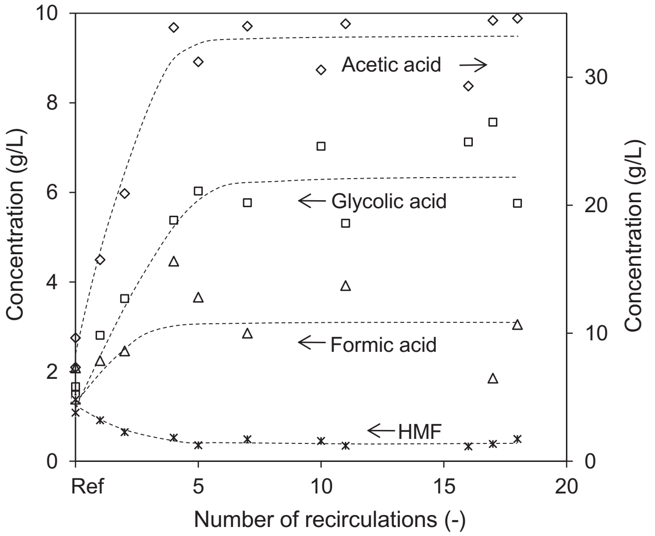

Fig. 2. Concentrations of identified substances for the number of process water recirculations.

a transport controlled reaction as e.g. emulsion polymerization (Wang et al., 2002).

Eight substances were identified by the applied HPLC method. The concentrations are listed in Table 3. Four compounds are organic acids and four are monomers which are known to form during hydrothermal solvolysis of biomass (Inoue et al., 2008). Here the latter are referred to as *intermediates*. For the reference and recirculation experiments the identified substances made up 40% and 51%, respectively with regards to the TOC. Fig. 2 shows the accumulation of these compounds in recirculation experiments. It can be noted that the concentrations of the organic acids augmented during the first 5 recirculations and thereafter remained almost constant. In contrast, the concentration of HMF diminished. Thus the share of organic acids as part of the TOC augmented with acetic acid alone contributing almost 40%.

The accumulation ratio as defined in Eq. (3) can reveal the behavior of the single compounds during recirculation. As displayed in Table 3 it was slightly higher than 1 for the organic acids which means that they composed final reaction products which did not take part in reactions, remained dissolved and concentrated in the liquid phase. This is supported by experiments of pure acetic and levulinic acid at high temperatures which indicate that such substances are stable under hydrothermal conditions (Knežević et al., 2009). It is also consistent with Lu et al. (2013) who report that the concentration of aliphatic/alcoholic substances increased and that of aromatic substances and aldehydes decreased over time in carbonization experiences with microcrystalline cellulose.

An accumulation ratio slightly higher than 1 means that the amount of organic acids produced during the reaction increased slightly or was not altered by the presence of high acid concentrations in the recirculated process water. This is in contrast to observations of Lynam et al. (2011) who report a net consumption of acetic acid when pure acetic acid was added in experiments with

Table 3
Concentrations of identified substances, the percentages as part of TOC and the accumulation ratios according to Eq. (3) (mean values of two reference experiments and the last three recirculation experiments; uncertainties in parenthesis).

Substance	Organic acids				Intermediates				Not identified C
	Acetic acid	Glycolic acid	Levulinic acid	Formic acid	Phenol	HMF	Furfural	Glucose	
Concentration (g/L)									
HTC-Ref	8.5 (1.2)	1.57 (0.09)	0.37 (0.06)	1.73 (0.35)	0.57 (0.04)	1.23 (0.15)	0.16 (0.01)	0.18 (0.04)	8.7
HTC-Recirc	32.8 (1.7)	6.82 (0.54)	1.44 (0.00)	2.45 (0.49)	1.01 (0.04)	0.41 (0.05)	0.00	0.02 (0.02)	16.7
As part of TOC (%)									
HTC-Ref	23	3.5	1.3	3.1	3.0	4.8	0.7	0.5	60
HTC-Recirc	38	6.3	2.2	1.9	2.3	0.7	0.0	0.0	49
Accumulation ratio (−)									
r	1.10	1.24	1.11	0.40	0.50	0.09	0.00	0.03	0.55

loblolly pine. One exception, however, is formic acid whose concentration augmented less than expected. Here one explanation may be the dissociation to carbon dioxide and hydrogen (Knežević et al., 2009). Despite a fourfold gain of organic acids by recirculation, the pH of the liquid phase was 3.4 and remained constant.

The identified neutral monomeric substances, which are also known to be intermediates in the formation of the solid HTC coal, behaved differently. Their concentration rather declined. One exception was phenol, whose concentration approximately doubled. Yet, the accumulation ratio of 0.5 shows, that its concentration rose less than expected. The concentrations of the other identified substances decreased to very low values with accumulation ratios of almost zero. Only 40–50% of the TOC was identified. The remainder was aggregated in a group of *not identified* substances. It consists of both not identified monomeric substances but presumably a major fraction is of macromolecular nature. This is supported by hydrothermal carbonization experiments with olive mill wastewater, where 76% of the dissolved organic substance is assumed to consist of macromolecules (Poerschmann et al., 2013).

The concentration of the group of not identified substances approximately doubled by recirculation and was characterized by an accumulation ratio of 0.55. It thus rose less than organic acids and the dissolved organic carbon as a whole. It can be expected that parts of the not identified monomeric substances took part in polymerization reactions, too, and formed additional solid substance. It can be concluded that the concentrations of the three identified groups of substances, organic acids, intermediates, and not identified substances, showed distinct differences when process water was recirculated which presumably facilitates water treatment. Substances such as HMF and furfural are toxic substances and are known to have inhibiting effects on fermentation (Modig et al., 2002). A relative rise of organic acids compared to reactive compounds hence may facilitate anaerobic and aerobic treatment of the liquid phase. Especially formic and acetic acid can be metabolized quickly to methane by methanogenesis. Methane yields from anaerobic wastewater treatment are expected to rise further when process water is recirculated and may contribute to an enhancement of the overall efficiency of the process. Alternatively, higher concentrations may also facilitate potential isolation of valuable dissolved substances.

4.2. Composition of HTC coal

4.2.1. Recirculation and acidification

The molar ratios of raw biomass and of HTC coal samples are depicted in the form of a van Krevelen diagram in Fig. 3. In this type of diagram the change in Oxygen and Hydrogen content by dehydration and decarboxylation, which are the main reactions taking place during the HTC treatment, is represented by straight lines. By HTC typically H/C and O/C ratios decline and thus the carbon content in the sample rises. Raising the reaction temperature lowers these ratios (Lu et al., 2013). From Fig. 3 it can be noted that by recirculation the molar ratios diminished further which induces also a higher carbon content in the samples. Fig. 3 suggests that by water recirculation dehydration reactions were catalyzed. It is assumed that this was mainly provoked by the concentration gain of organic acids by recirculation. A rise of the calorific value by addition of acetic acid was recently reported (Lynam et al., 2011). It is known that the dehydration reaction of hexoses to HMF is catalyzed by organic acids which are produced during the reaction or by addition of such (Kuster, 1990; Xiang et al., 2004).

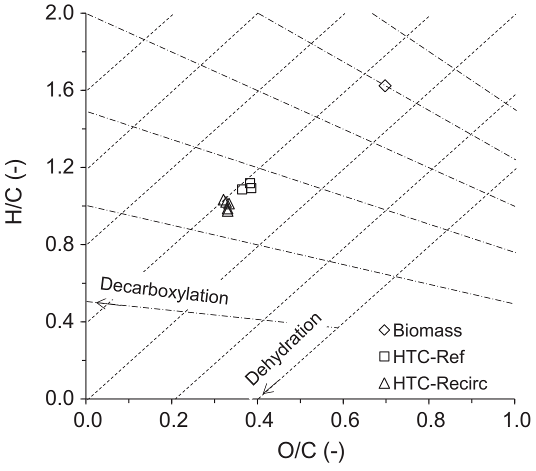

Fig. 3. Van Krevelen diagram with molar ratios of the raw material and of HTC coal samples from reference and recirculation experiments.

In order to verify the effect of organic acids at concentration levels found in recirculated water, experiments were performed where acetic acid, formic acid and glycolic acids were added at the same concentration levels as in the recirculated water when equilibrium was reached. Addition of organic acids had a similar effect on HTC coal as water recirculation (Fig. S-2). Both water recirculation and organic acid addition yielded a HTC coal with smaller H/C and O/C ratios (data not shown). The additional decline of H/C by the addition of organic acids compared to the reference experiments was 0.12 compared to 0.10 when water was recirculated. The additional decline of O/C for acid addition was 0.06 compared to 0.05 for recirculated water.

4.2.2. Mechanical dewatering

If HTC coal is to be incinerated it must be dewatered to a low water content in order to avoid energy intensive drying. Process water is chemically bound to the HTC coal especially by OH-groups. A decrease of functional groups thus leads to better dewaterability. Samples of HTC coal from reference experiments were mechanically dewatered by a laboratory piston press to a mean water content of 45.2 ± 1.1%. Dewatering at the same conditions yielded water contents of 35.6 ± 0.3% for samples from recirculation experiments. Significantly enhanced dewaterability by recirculation may thus raise the energetic performance of the HTC process.

4.2.3. Composition

IR-spectroscopy of the produced HTC coal samples revealed further insight with regards to the functional groups (Fig. S-3). It was observed that the peak between 3200 and 3600 cm^{-1}, which can be attributed to OH-groups, decreased by hydrothermal treatment. It diminished further when process water was recirculated. In analogy peaks at 898 cm^{-1} and 1050 cm^{-1} which can be associated with glycosidic bonds and cellulose macromolecules dropped. A significant drop of absorption of C_{alkyl}–O and C_{aryl}–O ether bonds 1031 cm^{-1} and 1236 cm^{-1}, respectively (Collier et al., 1992) may indicate a cleavage of ether bonds of the lignin macromolecule. It was observed that the addition of organic acids led to a similar reduction of the absorption peaks attributed to the functional groups. Presumably the rising concentration of organic acids provoked a decline of functional groups when water was recirculated.

Visually it was perceived in recirculation experiments that wood particles had collapsed after hydrothermal reaction whereas particle shapes remained intact when de-ionized water was used. Also a decline of the vibration of characteristic bonds of lignin and cellulose indicate further decomposition of macromolecules when process water was recirculated. This may further decrease the stability of pre-treated wood. During compression the porous structure is expected to break down. This may further facilitate compression and thus enhance mechanical dewatering yielding a lower water content.

4.3. Mass and energetic yields

As shown in Fig. 3 the addition of acid or the recirculation of process water resulted in further dehydration. Thus, by additional separation of hydrogen and oxygen, a lower mass yield would be expected. In fact this was observed in samples from the HTC experiments where organic acids were added. Here the mean solid mass yield decreased from 65.5 ± 0.5% to 62.0 ± 0.8% (data not shown). Yet, as shown in Table 4, the mass yield slightly augmented when process water was recirculated, which can be explained by additional polymerization of reactive substances. Due to a slight increment of the mass yield and a significant rise of the carbon content, the carbon yield rose significantly. This was also observed for the energetic yield and the calorific value.

Table 5 shows the amount of gasses formed during the reaction with respect to the amount of parent biomass. The gas phase was mainly composed of carbon dioxide. By recirculation the amount of gas formed increased by approximately 50%. The concentration of hydrogen in the gas phase increased tenfold. Matsumura et al. (2005) identify soluble organic substances as intermediates during the formation of the gas phase. As concentrations of soluble organic substances rose by recirculation this may explain the gain of collected gas.

Overall, by recirculation of process water, the yield of carbon in the liquid phase declined from 13.7 ± 0.8% to 7.7 ± 0.4%, whereas C-yields rose from 78.8 ± 0.7% to 83.9 ± 0.5% in the solid and from 5.1 ± 0.6% to 6.9 ± 0.4% in the gas phase.

As there are numerous assumed interactions of the recirculated substances with the liquid and solid phase, an overview is depicted in Fig. S-4. The experiments presented in this paper were reproduced with further biomass types including empty fruit bunches, bagasse and poplar leaves. Apart from small deviations the effects described above were observed for all biomass types. Altogether a series of positive effects may be expected from water recirculation. The sum of these effects seems to substantially enhance the overall performance of the process and thus should be considered when assessing the efficiency of hydrothermal carbonization as a whole.

5. Conclusions

HTC process water is very rich in organic carbon. The extractable TOC is of polar and aromatic nature. A major portion of the TOC is of higher molecular weight. By recirculation of process water, organic acids in the liquid phase accumulated and thus composed final reaction products. They catalyzed dehydration reactions and provoked a rise of the carbon content of the HTC coal and better dewaterability. Compounds of higher molecular weight are believed to have partially accumulated whereas reactive substances polymerized and formed additional solid substance. As a result carbon and energetic yields of the HTC coal increased.

Table 4
Elemental composition (on dry basis), solid mass yield, carbon yield, calorific value and energetic yield from reference and recirculation experiments (uncertainty in parenthesis).

	Wood	HTC-Ref	HTC-Recirc
C (%)	47.49	62.24 (0.30)	65.16 (0.10)
H (%)	6.42	5.61 (0.11)	5.49 (0.07)
N (%)	0.07	0.19 (0.06)	0.13 (0.01)
S (%)	0.05	0.03 (0.01)	0.05 (0.02)
Ash (%)	1.78	0.73 (0.03)	0.42 (0.01)
HHV[a] (MJ/kg)	19.5	25.0 (0.20)	26.2 (0.10)
Mass yield	–	0.601 (0.005)	0.612 (0.004)
C yield	–	0.788 (0.007)	0.839 (0.005)
Energetic yield (HHV)	–	0.770 (0.009)	0.819 (0.004)

[a] Calculated according to Channiwala and Parikh (2002).

Table 5
Gas yield and composition relative to the amount of parent biomass (g gas per kg of dry biomass).

	CO_2 (g/kg)	CO (g/kg)	CH_4 (g/kg)	H_2 (g/kg)
HTC-Ref	66	3.2	0.03	0.03
HTC-Recirc	101	5.0	0.04	0.42

Acknowledgements

This work has been funded by the German Federal Ministry of Education and Research as part of the joint research project 01LS0806B. HPLC analysis was performed by biopos e.V.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.05.098.

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